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Electronic Supplementary Information

Helical Polyisocyanide-based Macroporous Organic Catalysts for Asymmetric Michael Addition with High Efficiency and Stereoselectivity

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Measurements

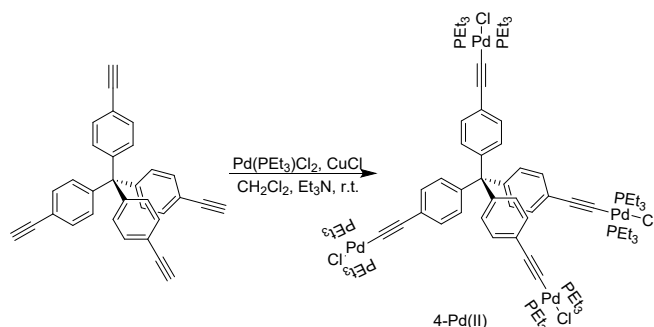
The NMR spectra were recorded using a Bruker 600 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of two linear TSK gel GMHHR-H columns. Molecular weight (M_n) and its dispersity (M_w/M_n) were reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FTIR system using KBr pellets. Circular dichroism (CD) spectra were obtained in a 1.0 or 0.1 cm quartz cell using a JASCO J1500 spectropolarimeter. The UV-vis absorption spectra were recorded on a UNIC 4802 UV/vis double beam spectrophotometer. The optical rotations were performed at 25 °C using a 10.0 cm quartz cell on a WZZ-2B polarimeter. High performance liquid chromatography (HPLC) with UV-vis detector was carried out on SHIMADZU LC-20AT equipment using chiral columns. Scanning electron microscopy (SEM) was performed on a SU8020 operating at 5.0 kV accelerating voltage. Nitrogen gas sorption experiments were carried out on Autosorb iQ Station 1 volumetric gas sorption instrument. Before measurement, the samples were degassed under vacuum at 80 °C for 12 h. The Brunauer Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the nonlocal density functional theory (DFT) model, the pore volume was derived from the sorption curve. X-ray diffraction measurements were conducted by using a Bruker D8 advance X-ray powder diffractometer with CuK_α (1.541 Å) radiation (40 kV, 40 mA) and samples were exposed at a scan rate of $2\theta = 0.02^\circ/\text{s}$ in the range between 3° and 40° . The benchtop time-domain NMR device (VTMR20-010V-I) was measured to the spin-spin relaxation time (T_2). The concentration of Pd in C-poly-**1**_ms and C-poly-**3**_ms were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) NexION 350X device.

Materials

All solvents were obtained from Sinopharm. Co. Ltd., and were purified by the standard procedures before use. All chemicals were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. The Pd(II) catalyst, 4-Pd(II), isocyanide monomer **1**, cross-linker **2**, and linear poly-**1**₁₅₀ were prepared according to the procedures reported by our group previously, and the structure was confirmed by ¹H NMR, ¹³C NMR spectra, FT-IR and MS m/z.^{1,2}

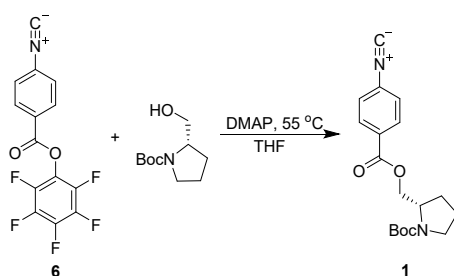
Synthetic procedures

Scheme S1. Synthesis of 4-Pd (II) catalyst.



Synthesis of 4-Pd(II) catalyat.¹ Tetrakis(4-ethynylphenyl)methane (200 mg, 0.49 mmol), *trans*-dichlorobis(triethylphosphine)palladium (820 mg, 2.0 mmol), and cuprous(I) chloride (2.5 mg, 0.025 mmol) were dissolved in the mixture of triethylamine (10 mL) and dichloromethane (10 mL) under dry nitrogen atmosphere. The mixture was stirred at room temperature for 2 h, then the solvent was removed by evaporation under reduced pressure. The afforded residue was purified by chromatography using petroleum ether as eluent. The crude product was recrystallized from petroleum ether and methanol to afford the expected 4-Pd(II) catalyst as a white solid (633 mg, 62% yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.13–7.08 (d, J = 6.0 Hz, 8H, ArH), 7.09–7.07 (d, J = 6.0 Hz, 8H, ArH), 1.98–1.96 (m, 12H, CH₂), 1.23–1.18 (m, 18H, CH₃).

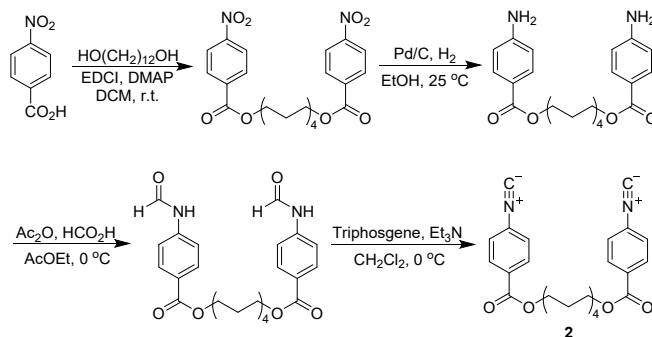
Scheme S2. Synthesis of monomer 1



Synthesis of monomer 1:² The monomer **1** was synthesized according to Scheme S2. isocyanide monomer (**6**) carrying pentafluorophenol ester was first prepared followed the procedure reported by our group previously and the structure was confirmed by ¹H NMR.⁴ A mixed solution of monomer **6** (4.82 g, 15.2 mmol), *tert*-butyl-(*S*)-2-(hydroxymethyl)pyrrolidine-1-carboxylate (3.02 g, 15.4 mmol), and 4-*N,N*-dimethylaminopyridine (DMAP, 1.36 g, 11.2 mmol) in dry THF (20 mL) was stirred at 55 °C for 12 h under nitrogen atmosphere. Then the solvent was removed by evaporation under reduced pressure. The residue was re-dissolved in CH₂Cl₂ (25 mL) and washed with water (50 mL \times 2) and an aqueous solution of sodium bicarbonate (50 mL \times 2). The

organic layer was dried over magnesium sulfate (MgSO₄) and purified by flash column chromatography using petroleum ether and ethyl acetate as eluent (v/v = 8/1) to afford monomer **1** as a colorless oil (4.32 g, 87% yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.12–8.08 (d, *J* = 12.0 Hz, 2H, ArH), 7.46–7.43 (d, *J* = 12.0 Hz, 2H, ArH), 4.42–4.22 (m, 2H, OCH₂), 4.08 (m, 1H, NCH), 3.46–3.39 (m, 2H, NCH₂), 1.93–1.74 (m, 4H, CH₂), 1.44 (s, 9H, CH₃).

Scheme S3. Synthesis of Cross-linker **2**



Synthesis of cross-linker 2: As displayed in Scheme S3, cross-linker (**2**) was prepared according the reported literature and the structure was confirmed by ¹H NMR.³ ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.12–8.05 (d, *J* = 12.0 Hz, 4H, ArH), 7.53–7.37 (d, *J* = 6.0 Hz, 4H, ArH), 4.28 (t, *J* = 6.0 Hz, 4H, CO₂CH₂), 1.87–1.25 (m, 20H, CH₂).

Typical synthesis procedure for 4-poly-*I_m*s: These polymers were prepared according to Scheme 1 in the main text.³ Taking 4-poly-**1**₂₀₀ as an example. A 10 mL oven-dried flask was charged with monomer **1** (0.20 g, 0.61 mmol), 4-Pd(II) catalyst (1.50 mg, 7.59 × 10⁻⁴ mmol), dry CHCl₃ (3.0 mL) and a stir bar. The concentrations of monomer **1** and the 4-Pd(II) complex were 0.2 and 2.5 × 10⁻⁴ M, respectively ([**1**]₀/[Pd]₀ = 200). The reaction flask was then immersed into an oil bath at 55 °C and stirred overnight. After cooled to room temperature, the polymerization solution was precipitated into a large amount of *n*-hexane, collected by centrifugation, and dried in vacuum at room temperature overnight to afford 4-poly-**1**₂₀₀ as a brown solid (0.16 g, 81% yield). [α]²⁵_D = -218 (*c* = 0.20, THF). SEC: *M_n* = 72.5 kDa, *M_w*/*M_n* = 1.22. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.41 (br, 2H, ArH), 5.70 (br, 2H, ArH), 3.92 (br, 3H, OCH₂ and NCH), 3.36 (br, 2H, NCH₂), 1.75 (br, 4H, (CH₂)₂), 1.40 (br, 9H, CH₃). FT-IR (KBr, 25 °C, cm⁻¹): 2995 (ν_{C-H}), 1728 (ν_{C=O}), 1605 (ν_{C=N}).

Synthesis procedure for poly-*I*₁₅₀:² The methoxy phenylethynyl Pd(II) complex and linear polymer were synthesized according to the procedure reported by our group previously.

Typical synthesis procedure for C-poly-1_ms: These polymers were prepared according to Scheme 1 in the main text.³ Taking C-poly-1₂₀₀ as an example. A 10 mL oven-dried flask was charged with 4-poly-1₂₀₀ (160 mg), the solution of linker **2** in CHCl₃ (22.5 μL (*c* = 8.0 mg/mL), 0.18 mg, 3.9 × 10⁻⁴ mmol), dry CHCl₃ (2.0 mL) and a stir bar. The reaction flask was then immersed into an oil bath at 55 °C and stirred overnight. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, the precipitated solid was collected by centrifugation, and dried in vacuum at room temperature overnight to afford C-poly-1₂₀₀ as a brown solid (152 mg, 98% yield). After dissolving the collected polymer in benzene (10.0 mL), it was freeze-dried for 24 hours, and afforded the desired C-poly-1₂₀₀. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.41 (br, 2H, ArH), 5.70 (br, 2H, ArH), 3.92 (br, 3H, CHCH₂), 3.36 (br, 2H, NCH₂), 1.75 (br, 4H, (CH₂)₂), 1.41 (br, 9H, CH₃). FT-IR (KBr, 25 °C, cm⁻¹): 2998 (ν_{C-H}), 1735 (ν_{C=O}), 1612 (ν_{C=N}).

Typical synthesis procedure for C-poly-3_ms: Taking C-poly-3₁₅₀ as an example.² C-poly-1₁₅₀ (150 mg) was dispersed in dry CH₂Cl₂ (5.0 mL), trifluoroacetic acid (TFA, 0.5 mL) was slowly added to the stirring solution at 0 °C. After the resulting suspension was stirred at room temperature overnight, the solution was adjusted to pH = 8.5 by ammonium hydroxide. After concentrated to dryness, the resulting residue was dissolved in MeOH (2.0 mL), then the suspension was washed with copious amounts of ether, collected by centrifugation, and dried in vacuum at room temperature overnight to afford the desired C-poly-3₁₅₀ as a yellow solid. (88.9 mg, 85% yield). ¹H NMR (600 MHz, CD₃OD, 25 °C): δ 7.40 (br, 2H, ArH), 6.85 (br, 1H, NH), 5.91 (br, 2H, ArH), 4.27 (br, 1H, CH), 3.75 (br, 2H, CH₂), 2.04 (br, 4H, (CH₂)₂). FT-IR (KBr, 25 °C, cm⁻¹): 3220 (ν_{N-H}), 2925 (ν_{C-H}), 1720 (ν_{C=O}), 1588 (ν_{C=N}).

General procedure for Michael addition reaction: Polymer catalyst C-poly-3₁₅₀ with 30% loading (with respect to repeating units) was added to the stirring solution of cyclohexanone (0.80 mmol) in expected solvent.⁴ Nitrostyrene (0.20 mmol) was added to this solution, and the resulting solution was stirred at a specific temperature indicated in Table 2 in the main text. After the reaction was accomplished, diethyl ether was added to the solution which caused the polymer catalyst precipitated. After centrifugation to remove the solid, the solution was concentrated under reduced pressure and the crude product was purified by preparative thin layer chromatography (TLC) on silica gel using petroleum ether and ethyl acetate as an eluent to afford the product. Taking the reaction of cyclohexanone with nitrostyrene as an example. C-poly-3₁₅₀ (20.0 mg, 0.06 mmol, with respect to repeating units) was added to the stirring solution of cyclohexanone (8.0 mg, 0.80 mmol) in brine. Then nitrostyrene (29.6 mg, 0.20 mmol) was added to this solution via a microsyringe. The resulting solution was stirred at room temperature and followed by thin layer chromatography (TLC). After the reaction was accomplished, diethyl ether was added to the solution which caused the polymer catalyst precipitated. After centrifugation to remove the solid, the solution was concentrated under reduced

pressure and the crude product was purified by preparative thin layer chromatography (TLC) on silica gel using petroleum ether and ethyl acetate as an eluent to afford the product.

NMR relaxation measurement. ^[5,6] The C-poly-**3**₁₅₀ was immersed in deionized water prior to NMR relaxation measurements. The C-poly-**3**_m was left in water for at least 24 h. Concentrations 10 wt % of C-poly-**3**₁₅₀ in water were prepared for the NMR relaxation measurements. A homogeneous and stable suspension without aggregation of C-poly-**3**₁₅₀ particles was prepared by mixing the samples in an ultrasonic bath until visible particle agglomerates disappeared. The temperature of the device was stabilized at 25 °C with an external thermostat during the measurements. Measurements were performed by measuring the suspensions in 5 mm NMR tubes. T_2 was determined using the “T2Bulk” method, which is based on the CPMG method. For this method, 5 Scans were used, a repetition time of 1 min, 50000 echoes and a CPMG echo time of 1 ms.

Wetted surface area calculated from NMR relaxation. the NMR relaxation time can be converted into the surface area by means of a straightforward calculation.

$$R_{av} = p_s R_s + p_b R_b$$

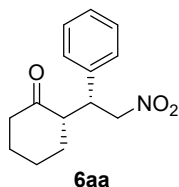
$$R_{av} = \psi_p S L \rho_p [R_s - R_b] + R_b$$

where p_s and p_b are the fractions of solvent in the bulk and surface respectively. R_s is the relaxation rate for the bound liquid, and R_b is the relaxation rate for the free or bulk liquid. Defining the spin relaxation rate constant R_s and R_b as the reciprocal of the spin relaxation time T_s and T_b . where R_{av} is the average spin relaxation rate. ψ_p is the particle volume to liquid volume ratio; S is the total surface area per unit mass; ρ_p is the bulk particle density; L is the thickness of the liquid surface layer. It is commonly assumed that L is a single solvent diameter though there.

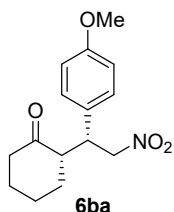
Kinetic studies. A stirred solution of *trans*-nitrostyrene (30.0 mg, 0.2 mmol), internal standard 1,4-dimethoxybenzene (7.0 mg, 0.05 mmol), and cyclohexanone (78.7 mg, 0.8 mmol) were added to a solution of polymer catalyst in brine (1.0 mL) with 10 mol% catalyst loading. The reaction solution was stirred at -10 °C for one week. A series of aliquots were taking out from the reaction solution at appropriate time intervals for further analyses. The conversion of substrate *trans*-nitrostyrene was calculated based on the peak area of unreacted *trans*-nitrostyrene relative to that of the internal standard 1,4-dimethoxybenzene on the basis of the linear calibration curve.

Other Michael addition reactions were performed under the similar procedure and the characterization data for the products are showed below.

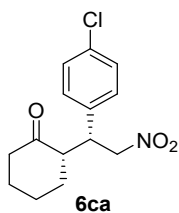
Characterization data for Michael addition products



(*S*)-2-((*R*)-2-nitro-1-phenylethyl)cyclohexanone (**6aa**): ^1H NMR (600 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 7.33 (d, $J = 6.0$ Hz, 2H), 7.32–7.25 (m, 2H), 7.17–7.16 (m, 1H), 4.95–4.92 (m, 1H), 4.70–4.66 (m, 1H), 4.02–3.98 (m, 0.1H, *anti* CH), 3.78–3.75 (m, 0.9H, *syn* CH), 2.75–2.71 (m, 1H), 2.70–2.66 (m, 1H), 2.45–2.37 (m, 1H), 2.27–2.18 (m, 1H), 2.04–1.82 (m, 4H), 1.59–1.53 (m, 1H). The enantiomeric excess (*ee*): 99%, and diastereomeric ratio (*dr*): 92/8 values were determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (*n*-hexane/2-propanol = 90/10, v/v), at an eluent rate of 1.00 mL/min; t_{R1} (*anti.*) = 15.37 min, t_{R2} (*anti.*) = 20.35 min, t_{R1} (*syn.*) = 20.90 min, t_{R2} (*syn.*) = 24.33 min.

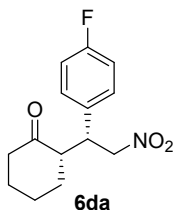


(*S*)-2-((*R*)-1-(4-methoxyphenyl)-2-nitroethyl)cyclohexanone (**6ba**): ^1H NMR (600 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 7.18 (d, $J = 12.0$ Hz, 2H), 6.92 (d, $J = 6.0$ Hz, 2H), 4.92–4.87 (m, 1H), 4.70–4.64 (m, 1H), 4.09 (s, 0.12H, *anti* CH), 4.06 (s, 3H), 4.01–3.95 (m, 0.91H, *syn* CH), 3.11–2.97 (m, 1H), 2.87–2.80 (m, 1H), 2.78–2.68 (m, 1H), 2.46–2.33 (m, 1H), 2.15–1.99 (m, 4H), 1.71–1.59 (m, 1H). The *ee*: 99%, and *dr*: 90/10, determined by chiral HPLC with a Chiralpack AD-H column at 254 nm (*n*-hexane/2-propanol = 80/20, v/v), at an eluent rate of 0.50 mL/min; t_{R1} (*anti.*) = 17.79 min, t_{R2} (*anti.*) = 19.87 min, t_{R1} (*syn.*) = 21.86 min, t_{R2} (*syn.*) = 23.52 min.

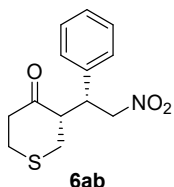


(*S*)-2-((*R*)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexanone (**6ca**): ^1H NMR (600 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 7.30 (d, $J = 12.0$ Hz, 2H), 7.16 (d, $J = 6.0$ Hz, 2H), 4.93–4.87 (m, 1H), 4.75–4.68 (m, 1H), 4.08–3.98 (m, 0.04H, *anti* CH), 3.87–3.78 (m, 0.99H, *syn* CH), 2.83–2.70 (m, 1H), 2.61–2.54 (m, 1H), 2.54–2.43 (m, 1H), 2.14–2.03 (m, 1H), 1.90–1.76 (m, 4H), 1.55–1.41 (m, 1H). The *ee*: 99%, *dr*: 97/3, determined by chiral HPLC with a Chiralpack AD-H column at 254 nm (*n*-hexane/2-propanol = 90/10, v/v), at an eluent rate

of 0.50 mL/min; t_{R1} (*anti.*) = 12.26 min, t_{R2} (*anti.*) = 13.37 min, t_{R1} (*syn.*) = 15.32 min, t_{R2} (*syn.*) = 18.53 min.



(*S*)-2-((*R*)-1-(4-fluorophenyl)-2-nitroethyl)cyclohexanone (**6da**): ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ 7.20 (d, J = 12.0 Hz, 2H), 7.02 (d, J = 6.0 Hz, 2H), 4.95–4.90 (m, 1H), 4.75–4.69 (m, 1H), 4.08–4.04 (m, 0.05H, *anti* CH), 3.96–3.85 (m, 1.00H, *syn* CH), 2.89–2.74 (m, 1H), 2.64–2.58 (m, 1H), 2.57–2.44 (m, 1H), 2.38–2.25 (m, 1 H), 2.11–1.70 (m, 4H), 1.52–1.38 (m, 1H). The *ee*: 99%, *dr*: 94/6, determined by chiral HPLC with a Chiralpack AD-H column at 254 nm (*n*-hexane/2-propanol = 75/25, v/v), at an eluent rate of 0.70 mL/min; t_{R1} (*anti.*) = 10.79 min, t_{R2} (*anti.*) = 12.04 min, t_{R1} (*syn.*) = 12.99 min, t_{R2} (*syn.*) = 13.93 min.



(*S*)-tetrahydro-3-((*R*)-2-nitro-1-phenylethyl)thiopyran-4-one (**6ab**): ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ 7.34 (d, J = 12.0 Hz, 2H), 7.35 (m, 1H), 7.18 (d, J = 6.0 Hz, 2H), 4.94–4.85 (m, 2H), 4.65–4.55 (t, 1H), 4.08–4.03 (m, 1H), 3.87–3.60 (m, 4H), 3.36–3.27 (t, 1H), 3.05–2.98 (m, 1H), 2.85–2.74 (m, 1H), 2.73–2.66 (m, 1H). The *ee*: 99%, *dr*: 99/1, determined by chiral HPLC with a Chiralpack AD-H column at 254 nm (*n*-hexane/ 2-propanol = 85/15, v/v), at an eluent rate of 1.00 mL/min; t_{R1} (*syn.*) = 14.92 min, t_{R2} (*syn.*) = 16.32 min, t_{R1} (*anti.*) = 30.73 min, t_{R2} (*anti.*) = 32.73 min. where q_e (mg/g) is the amount of iodine adsorbed at equilibrium time, $q_{max,e}$ (mg/g) is the maximum adsorption capacity of C-poly-**1**₅ at equilibrium, K (mol^{-1}) is the equilibrium constant and c (mol/L) is the residual iodine concentration at equilibrium.

Table S1. Characterization Data for 4-poly-**1**_ms^a

run	polymers	M_n^b (kDa)	M_w/M_n^b	Yield ^c	$\theta_{364}(\times 10^3)^d$	$[\alpha]^{25}_D^e$
1	4-poly- 1 ₂₀	13.8	1.19	89%	-6.15	-118
2	4-poly- 1 ₅₀	22.0	1.22	92%	-9.37	-172
3	4-poly- 1 ₈₀	30.5	1.23	91%	-11.58	-190
4	4-poly- 1 ₁₀₀	38.1	1.22	89%	-13.02	-201
5	4-poly- 1 ₁₅₀	57.9	1.24	90%	-14.29	-210
6	4-poly- 1 ₂₀₀	72.5	1.22	81%	-14.51	-218

^aThe polymers were synthesized according to Scheme 1 in the main text. ^bThe M_n and M_w/M_n were determined by SEC with equivalent to polystyrene standards. ^cIsolated yields. ^dThe CD intensity at 364 nm of 4-poly-**1**_ms measured in THF at 25 °C. ^eThe optical rotations of 4-poly-**1**_ms measured in THF at 25 °C.

Table S2. The recycled using of C-poly-**3**₁₅₀ in Michael addition reaction of cyclohexanone and *trans*-nitrostyrene^a

cycle	yield ^b (%)	<i>dr</i> ^c	<i>ee</i> ^d (%)
1	84	92/8	99
2	80	90/10	99
3	83	91/9	98
4	82	92/8	97
5	82	91/9	99
6	84	90/10	98

^aThe reactions were carried out with *trans*-nitrostyrene (0.20 mmol), cyclohexanone (0.80 mmol) in brine (1.0 mL) at 0 °C. ^bYield of isolated products. ^cThe *dr* values were determined by HPLC analysis using a chiral stationary phase. ^dThe *ee* (%) values were referred to the major isomer determined by HPLC analysis using a chiral stationary phase.

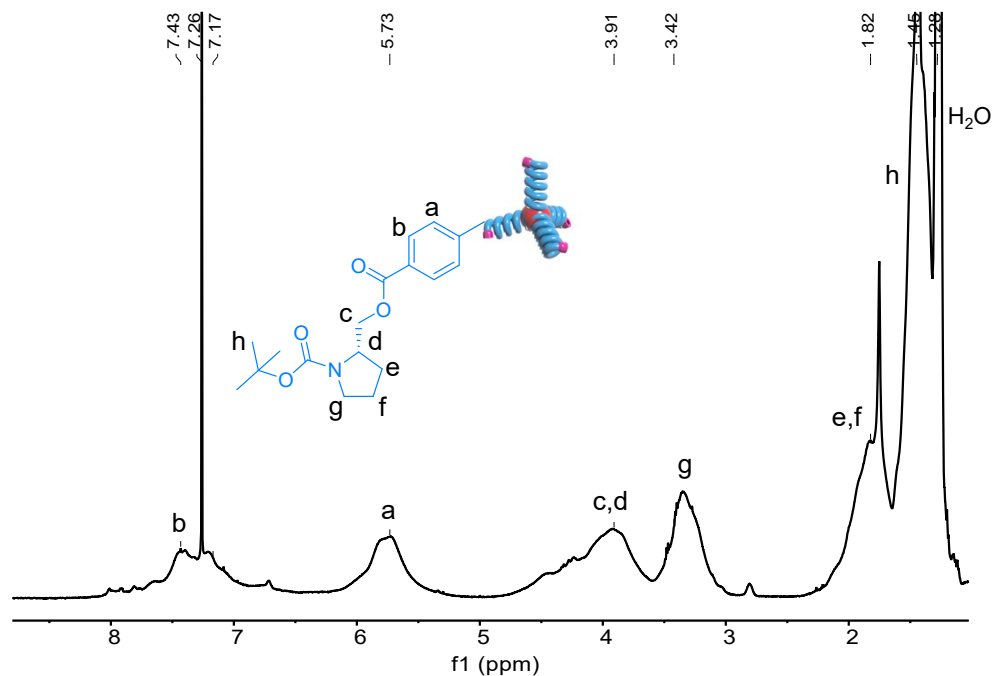


Figure S1. ^1H NMR (600 MHz) spectrum of 4-poly- 1_{20} measured in CDCl_3 at 25 °C.

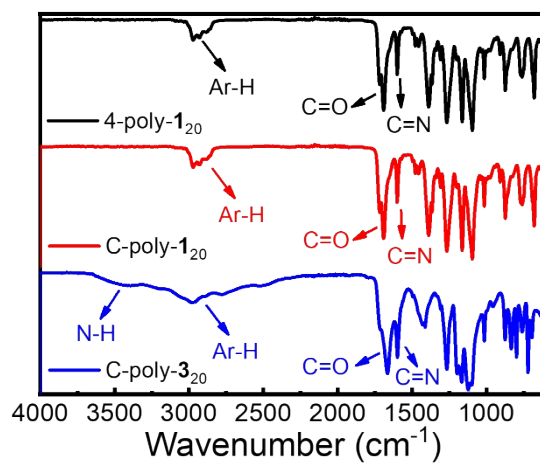


Figure S2. FT-IR spectra of 4-poly- 1_{20} , C-poly- 1_{20} and C-poly- 3_{20} measured at 25 °C using KBr pellets.

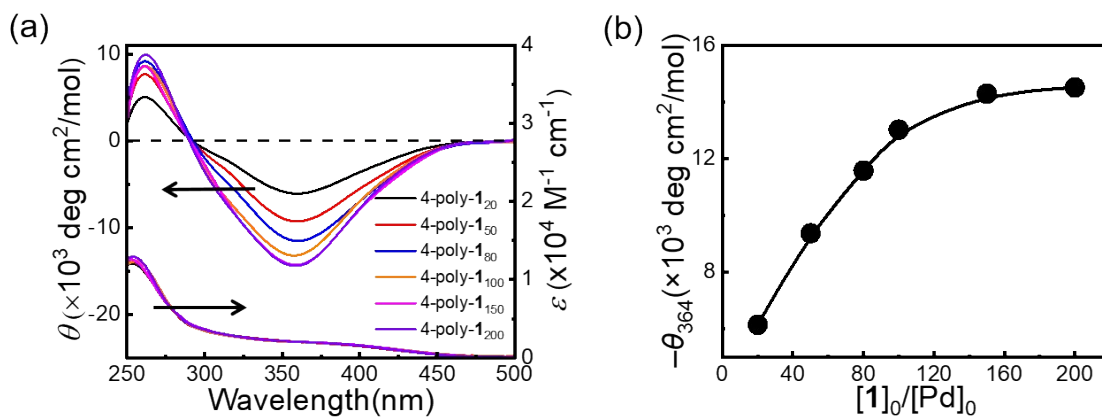


Figure S3. (a) CD and UV-vis spectra of 4-poly-1_ms measured in THF at 25 °C ($c = 0.2$ mg/mL). (b) Plots of ellipticity at 364 nm of 4-poly-1_ms as a function of the $[1]_0/[Pd]_0$.

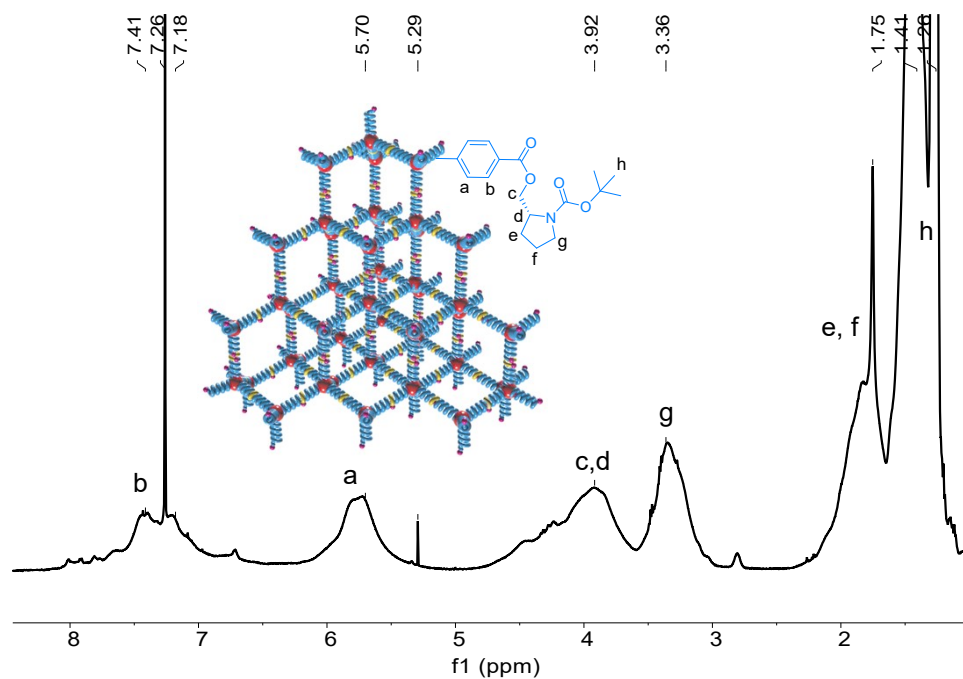


Figure S4. ¹H NMR (600 MHz) spectrum of C-poly-1₂₀ measured in CDCl₃ at 25 °C.

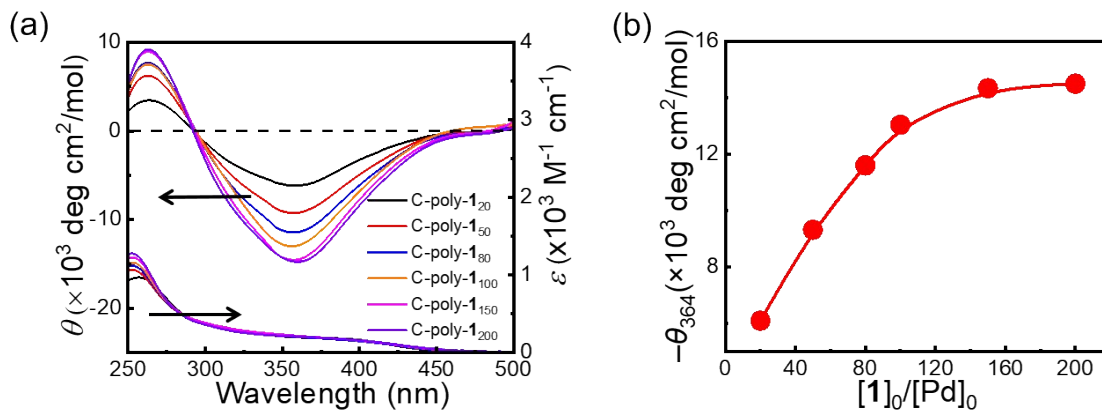


Figure S5. (a) The CD and UV-vis spectra of film state C-poly-1_{ms} at 20 °C. (b) Plots of ellipticity at 364 nm of C-poly-1_{ms} as a function of the $[1]_0/[Pd]_0$.

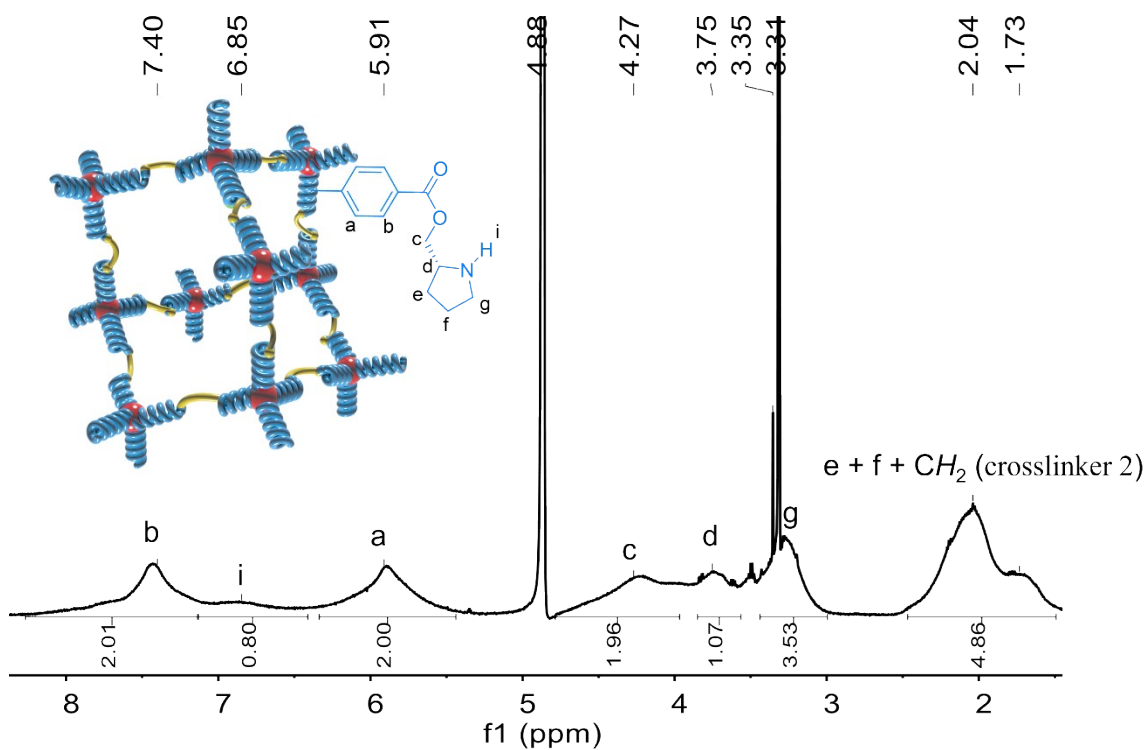


Figure S6. ^1H NMR (600 MHz) spectrum of C-poly-3₂₀ measured in CD_3OD at 25 °C.

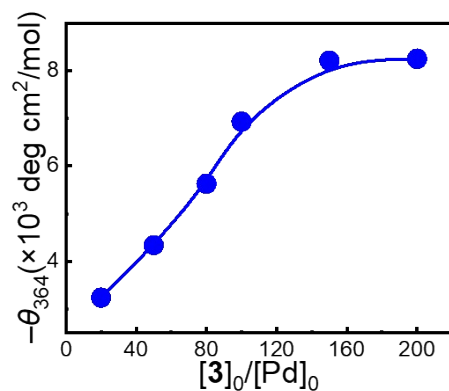


Figure S7. Plots of ellipticity at 364 nm of C-poly- $3_{m,s}$ as a function of the DP.

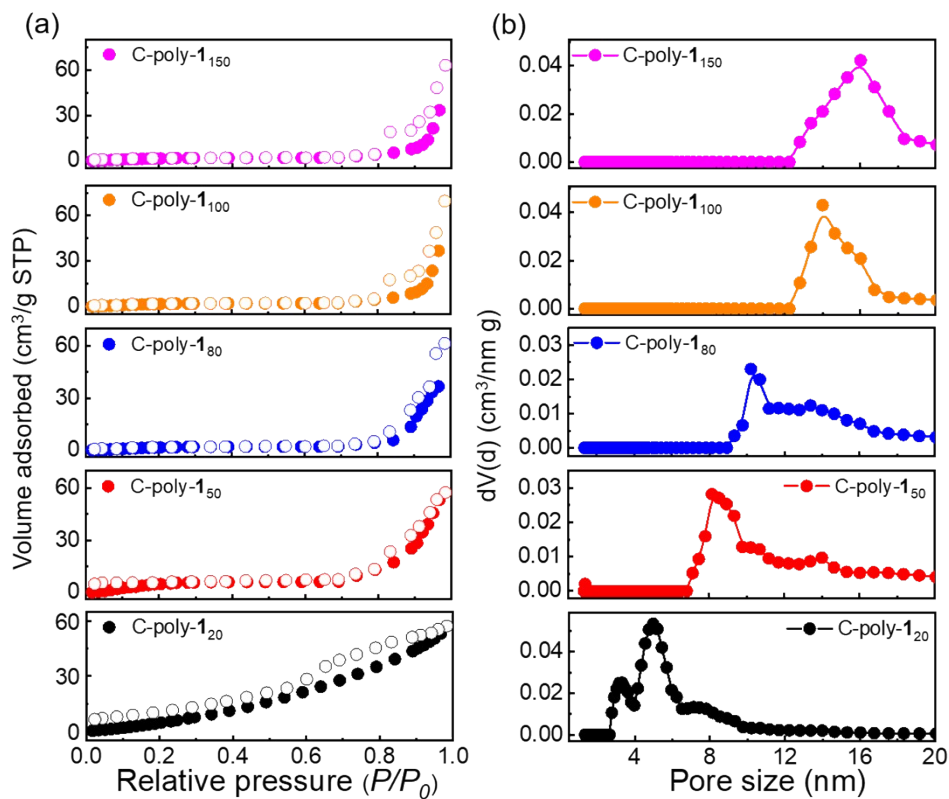


Figure S8. Nitrogen sorption isotherms (a), and pore size distributions (b) of C-poly- $1_{m,s}$ recorded at 77 K. Notably, the filled symbols denote gas adsorption while the empty symbols denote gas desorption in Figure (a).

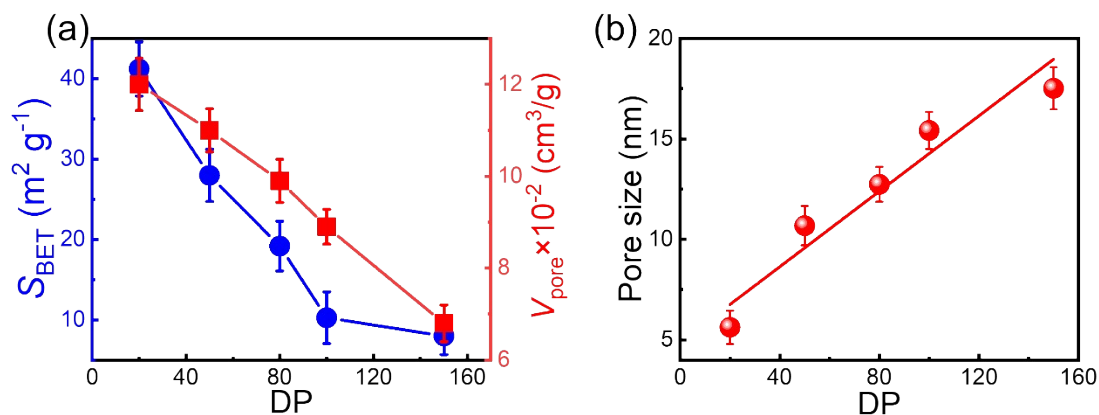


Figure S9. (a) Plots of S_{BET} and V_{pore} of C-poly-3_ms as a function of the DP of the polyisocyanide blocks. (b) Plots of pore size of C-poly-3_ms as a function of the DP of the polyisocyanide blocks.

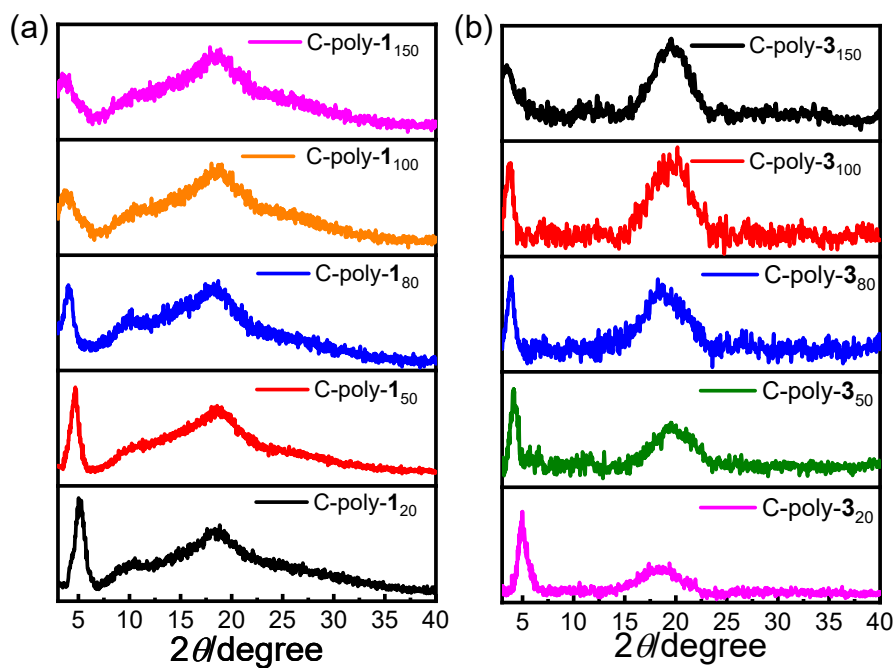


Figure S10. PXRD profiles of C-poly-1_ms (a) and C-poly-3_ms (b) with different lengths of polyisocyanide blocks.

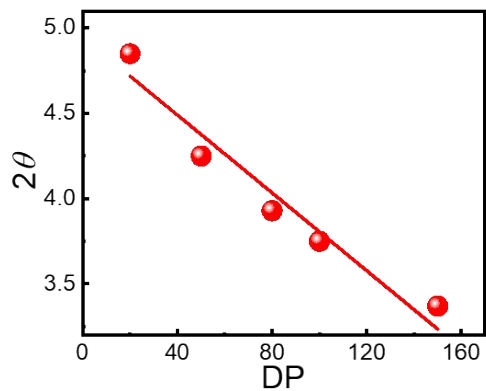


Figure S11. Plots of 2θ of C-poly-**3**_ms as a function of the DP of the polyisocyanide blocks.

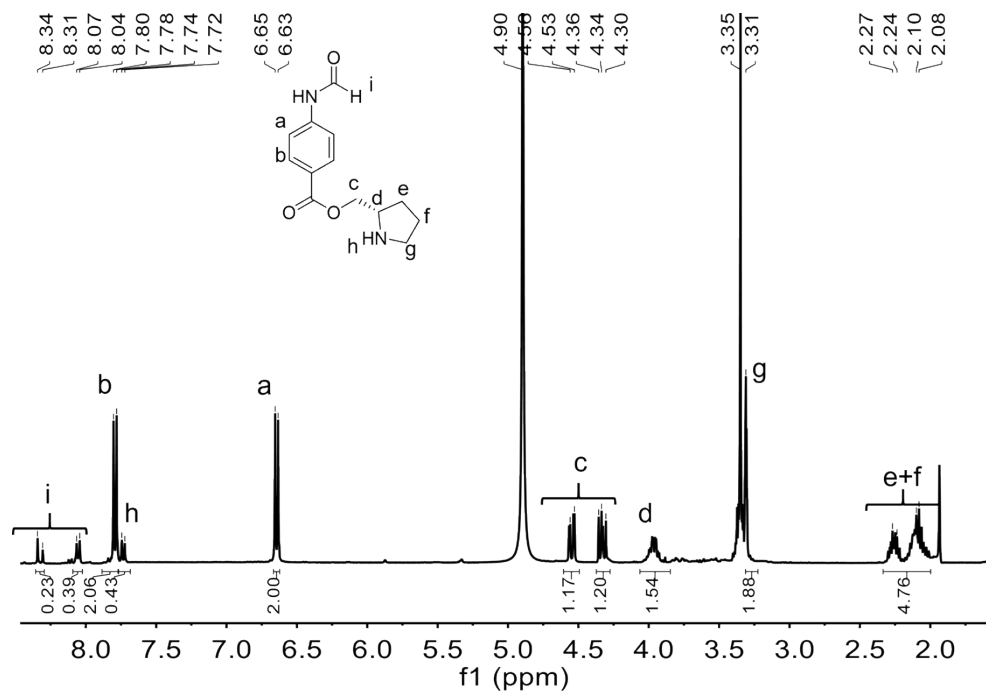


Figure S12. ^1H NMR (600 MHz) spectrum of compound **7** measured in CDCl_3 at 25°C .

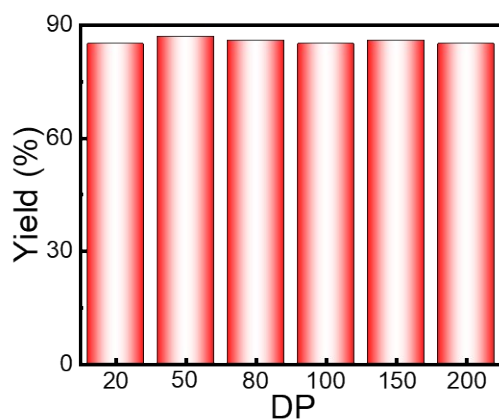


Figure S13. The yields of **6aa** catalyzed by C-poly-**3**_{ms} with different DPs of the polyisocyanide blocks.

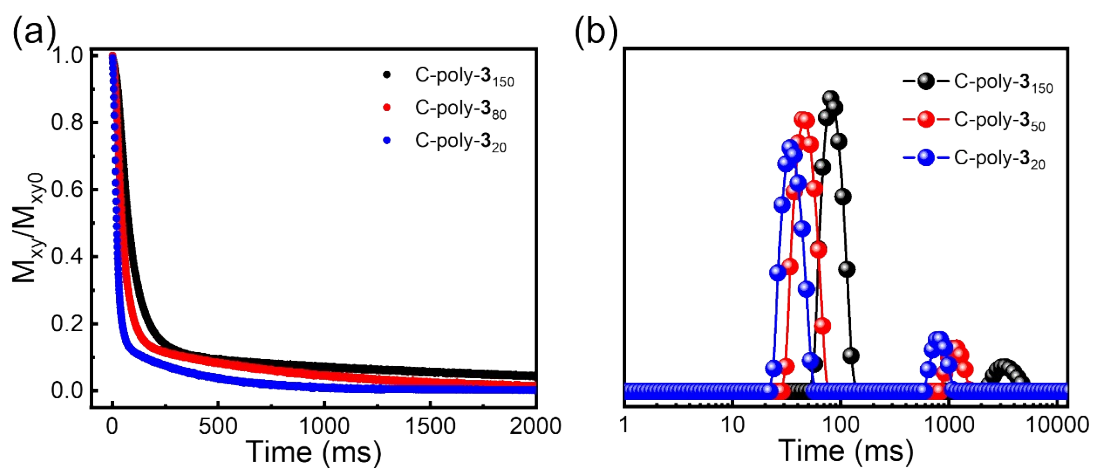


Figure S14. (a) T_2 relaxation curve of water in comparison to 10 wt % of C-poly-**3**_{ms} in water measured at 25 °C. (b) The T_2 distributions arising from the ordinary CPMG applied on the emulsions tempered to 25 °C.

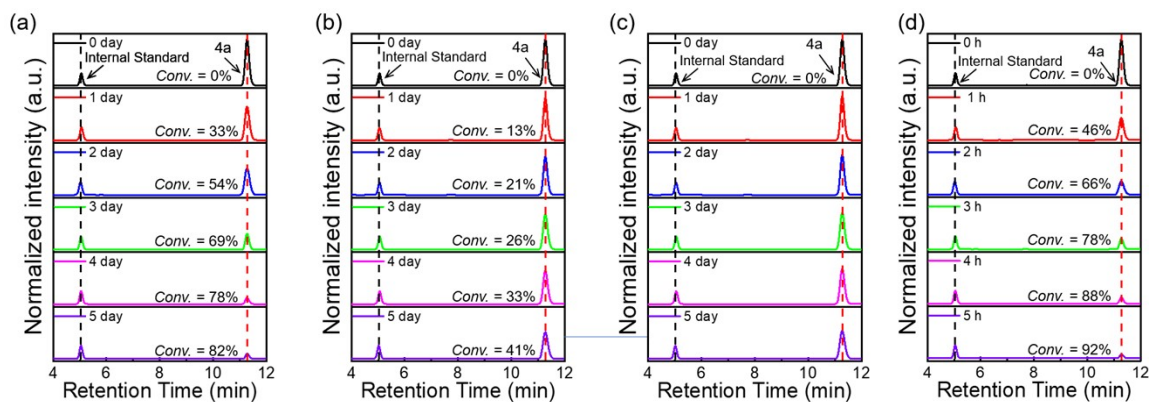


Figure S15. Time-dependent HPLC curves of *trans*-nitrostyrene catalyzed by C-poly-**3**₁₅₀ (a), poly-**3**₁₅₀ (b), C-poly-**3**₁₅₀ (c) and compound **7** (d) with the presence of 1,4-dimethoxybenzene as internal standard. HPLC conditions: column: AD-H; eluent: *n*-hexane/isopropanol = 9/1 (v/v); eluent rate: 0.75 mL/min.

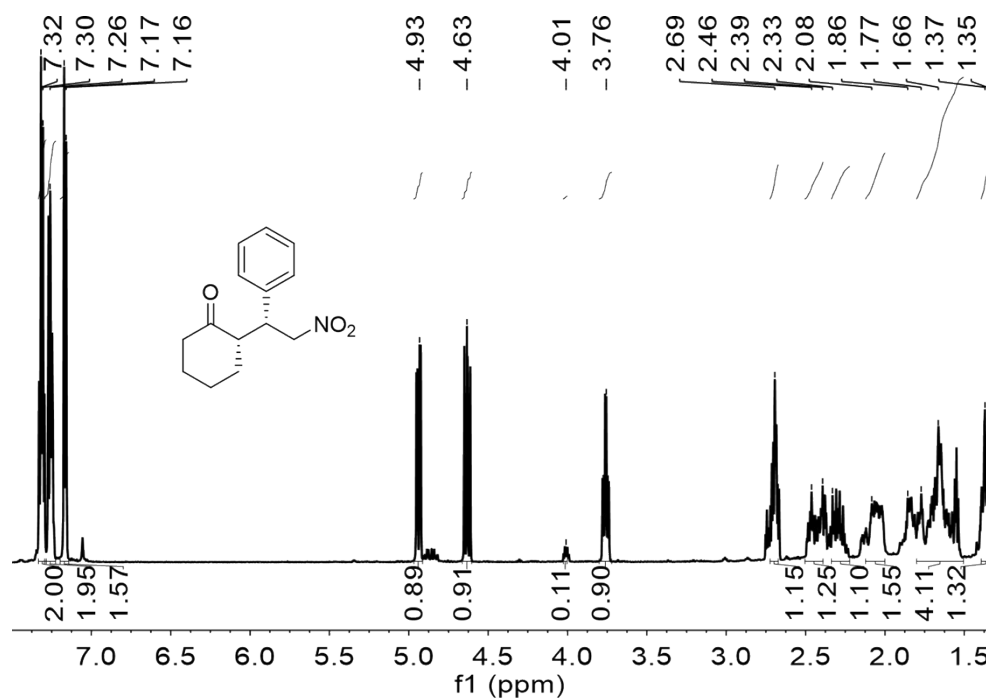


Figure S16. ¹H NMR (600 MHz) spectrum of (*S*)-2-((*R*)-2-nitro-1-phenylethyl)cyclohexanone (**6aa**) measured in CDCl₃ at 25 °C.

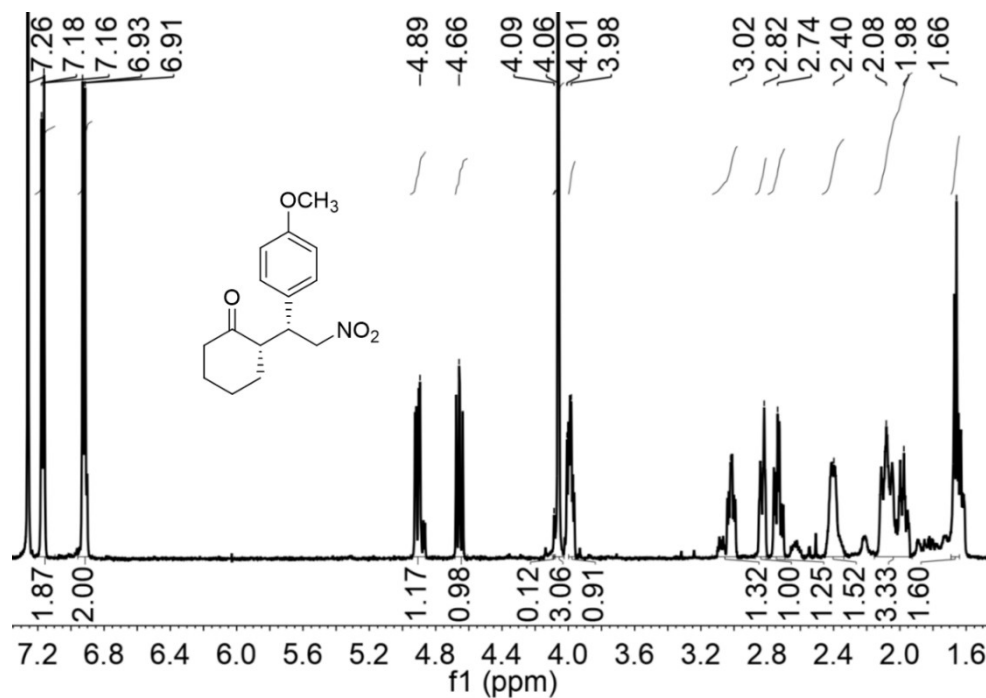


Figure S17. ^1H NMR (600 MHz) spectrum of (*S*)-2-((*R*)-1-(4-methoxyphenyl)-2-nitroethyl)cyclohexanone (**6ba**) measured in CDCl_3 at 25 °C.

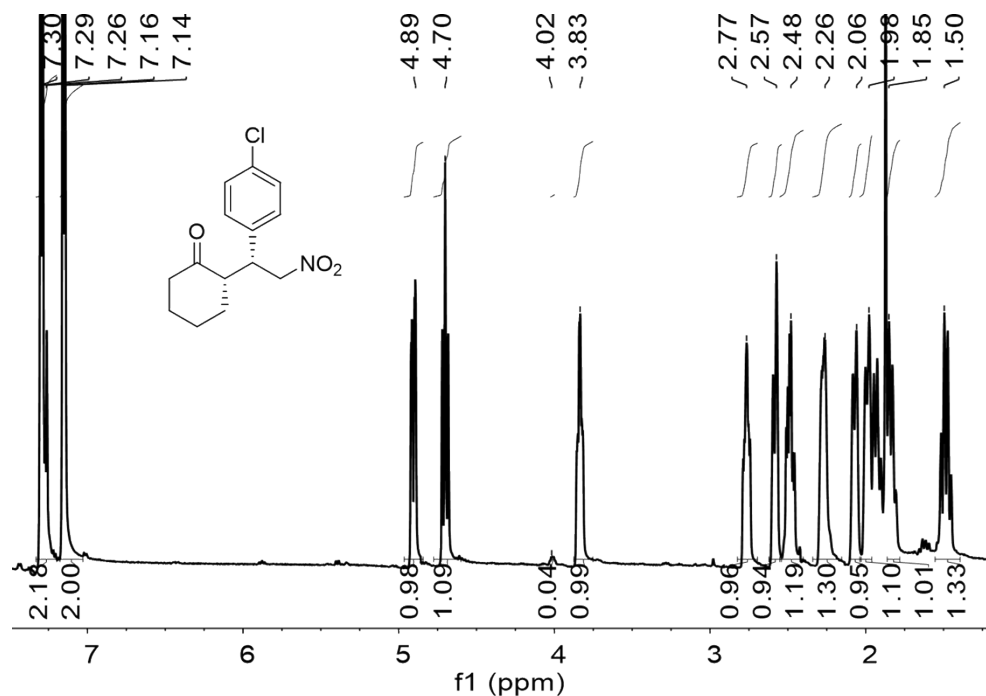


Figure S18. ^1H NMR (600 MHz) spectrum of (*S*)-2-((*R*)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexanone (**6ca**) measured in CDCl_3 at 25 °C.

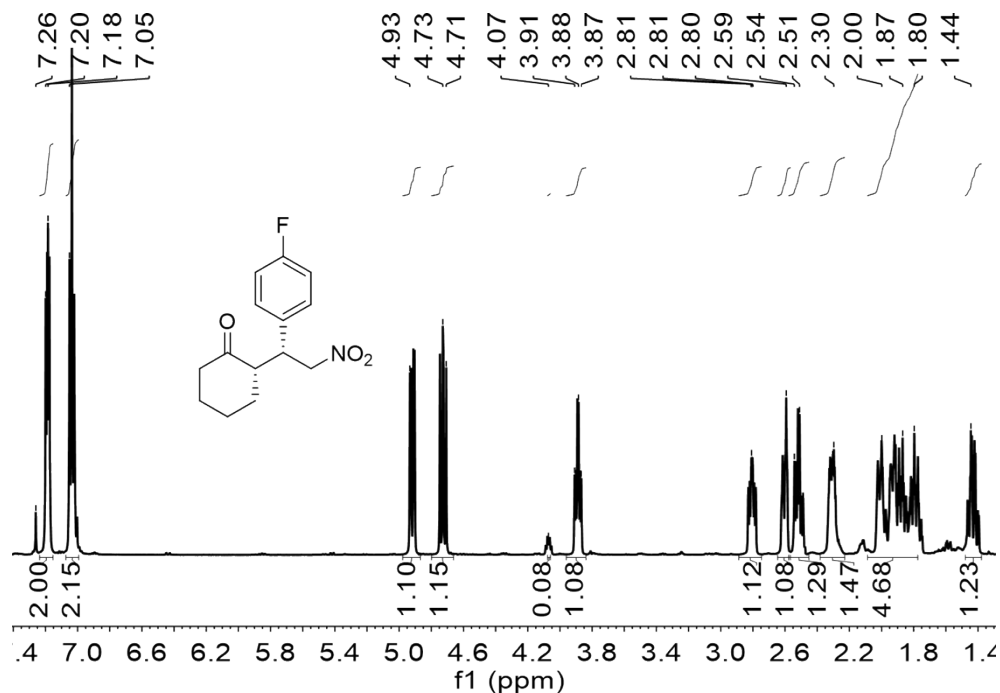


Figure S19. ^1H NMR (600 MHz) spectrum of monomer (*S*)-2-((*R*)-1-(4-fluorophenyl)-2-nitroethyl)cyclohexanone (**6da**) measured in CDCl_3 at 25 °C.

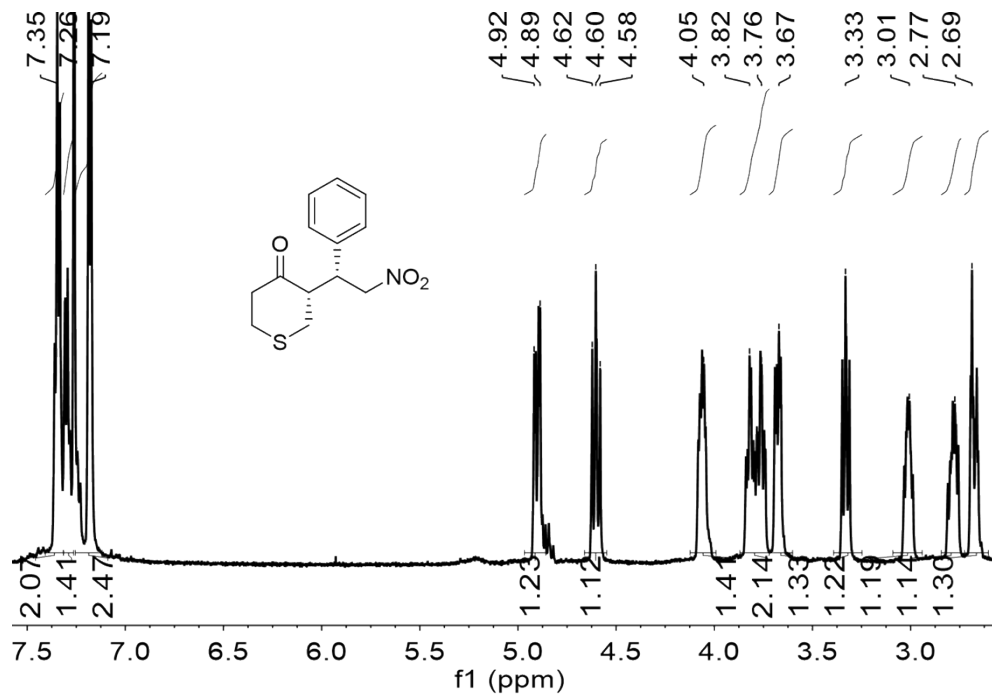


Figure S20. ^1H NMR (600 MHz) spectrum of (*S*)-tetrahydro-3-((*R*)-2-nitro-1-phenylethyl)thiopyran-4-one (**6ab**) measured in CDCl_3 at 25 °C.

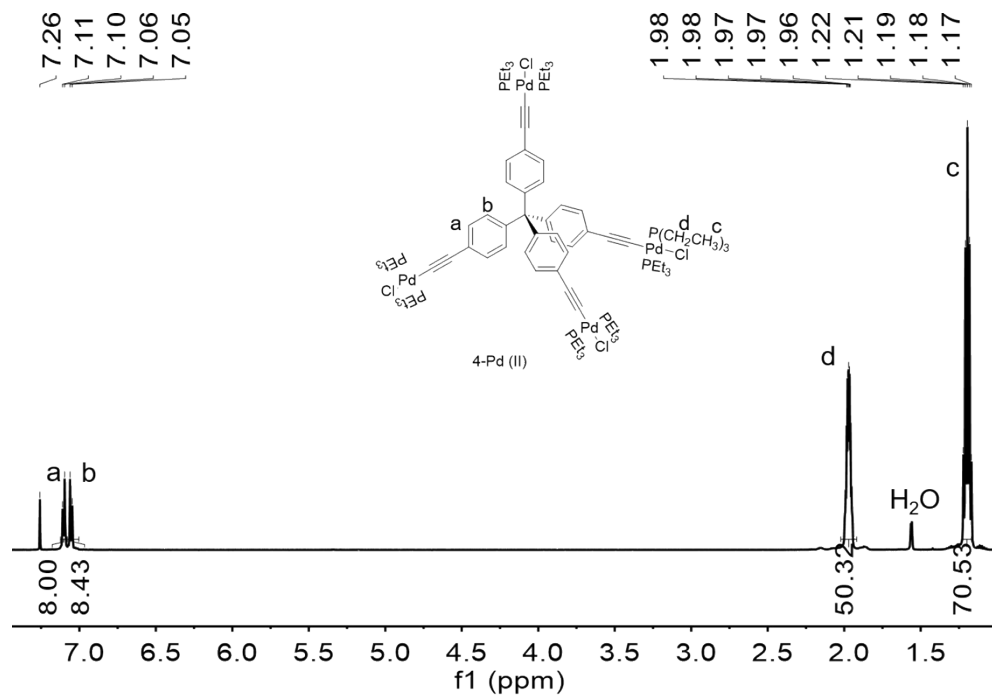


Figure S21. ^1H NMR (600 MHz) spectrum of 4-Pd(II) measured in CDCl_3 at 25 $^\circ\text{C}$.

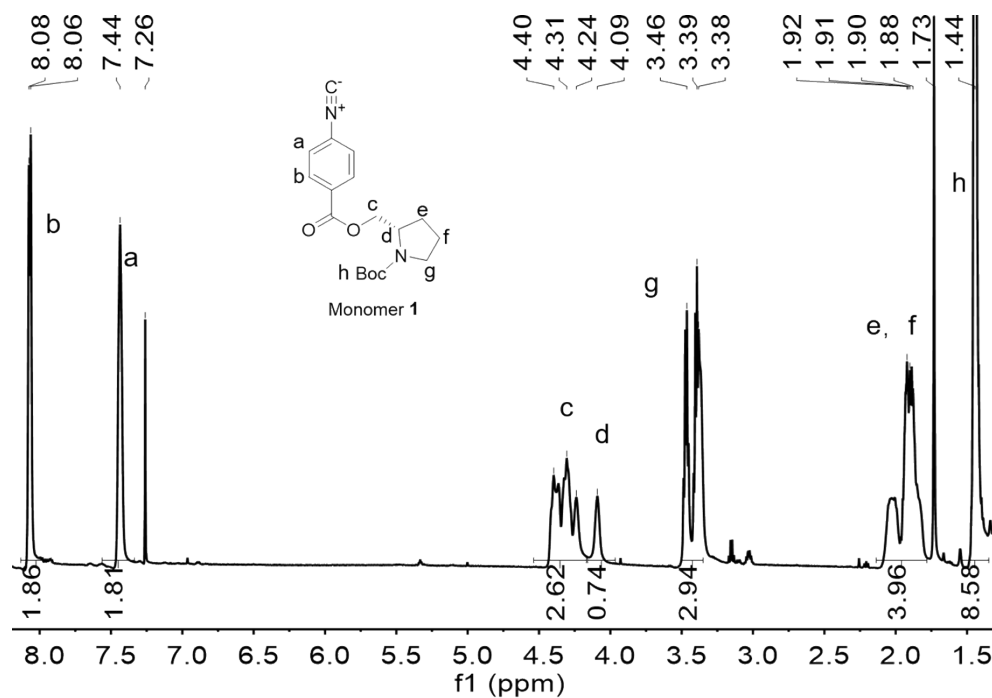


Figure S22. ^1H NMR (600 MHz) spectrum of monomer 1 measured in CDCl_3 at 25 $^\circ\text{C}$.

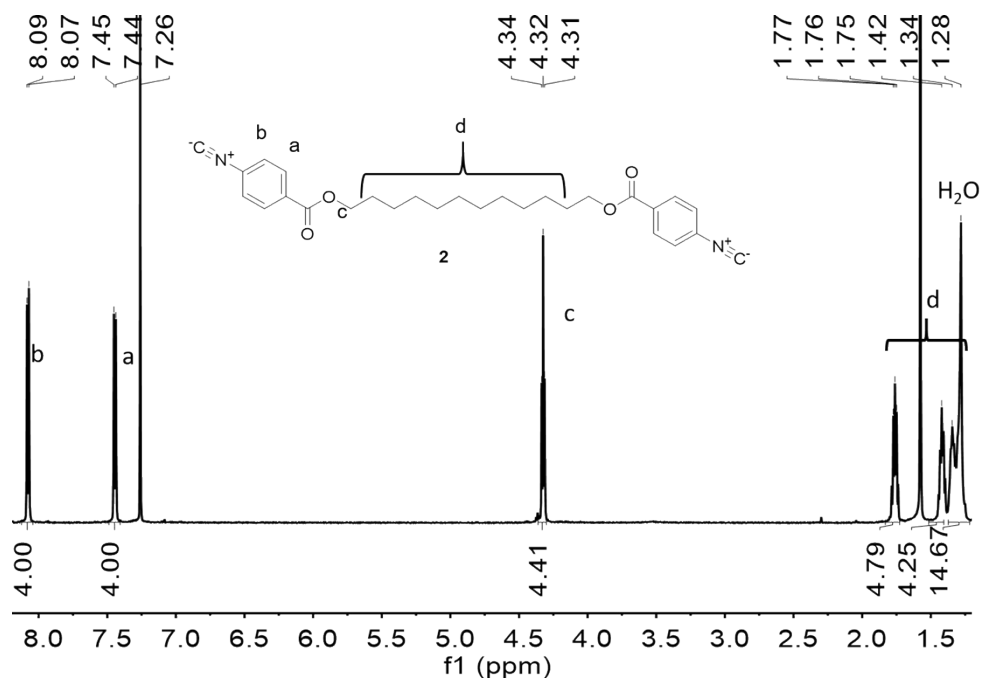


Figure S23. ^1H NMR (600 MHz) spectrum of cross-linker **2** measured in CDCl_3 at 25°C .

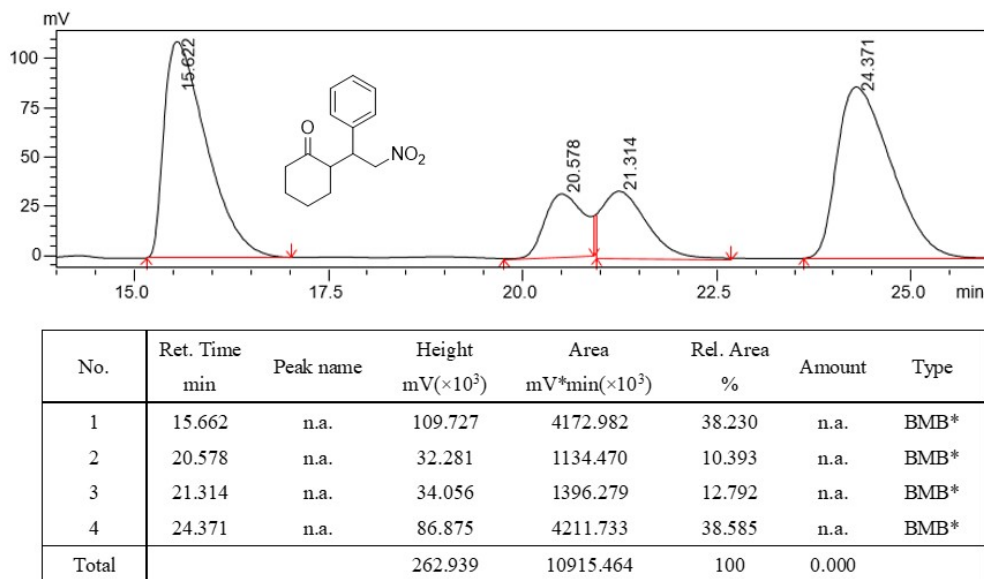


Figure S24. HPLC curve of racemic (2-nitro-1-phenylethyl)cyclohexanone (**6aa**) (Chiralpak AS-H; n -hexane/ i -PrOH = 90/10 (v/v); 1.00 mL/min; 254 nm; 25°C).

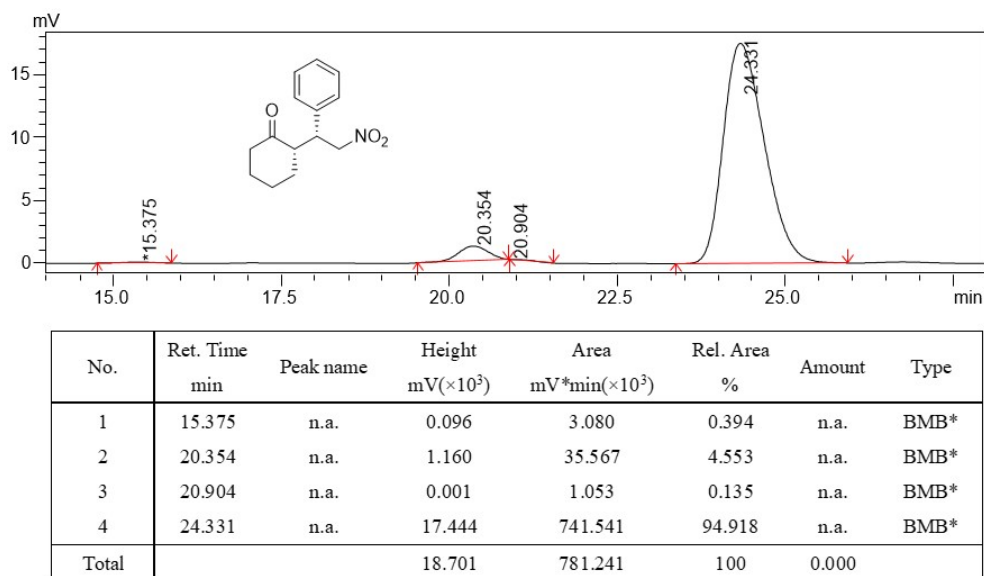


Figure S25. HPLC curve of (*S*)-2-((*R*)-2-nitro-1-phenylethyl)cyclohexanone (**6aa**) (Chiralpak AS-H; *n*-hexane/*i*-PrOH = 90/10 (v/v); 1.00 mL/min; 254 nm; 25 °C).

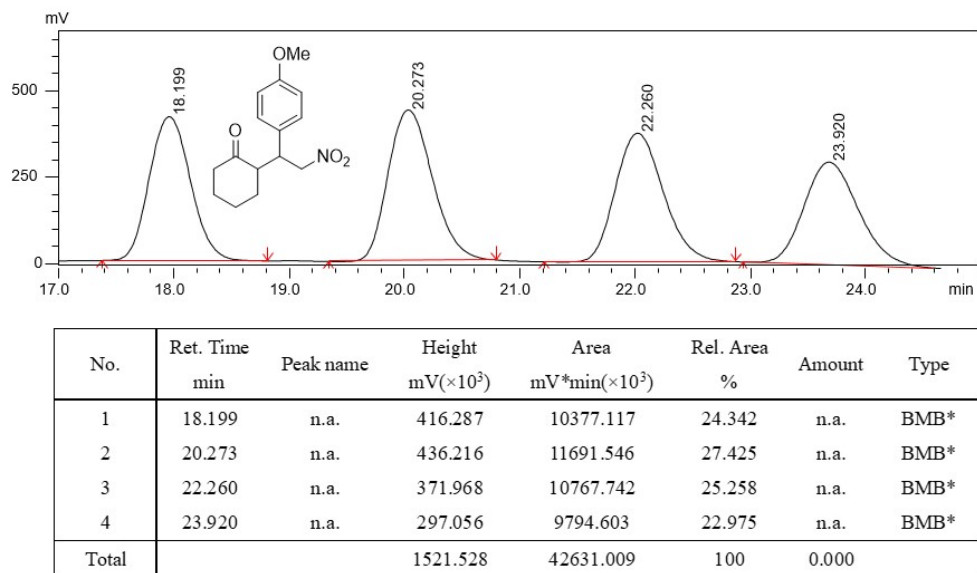
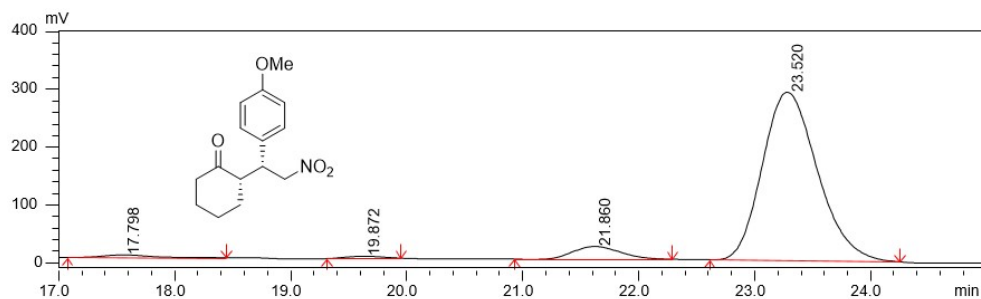
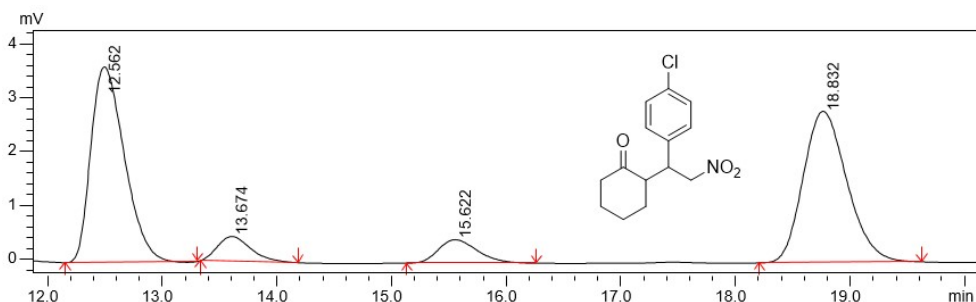


Figure S26. HPLC curve of racemic 1-(4-methoxyphenyl)-2-nitroethyl)cyclohexanone (**6ba**) (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 80/20 (v/v); 0.50 mL/min; 254 nm; 25 °C).



No.	Ret. Time min	Peak name	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %	Amount	Type
1	17.798	n.a.	1.456	55.097	0.620	n.a.	BMB*
2	19.872	n.a.	10.051	81.846	0.921	n.a.	BMB*
3	21.860	n.a.	21.264	346.314	3.897	n.a.	BMB*
4	23.520	n.a.	253.999	8395.441	94.472	n.a.	BMB*
Total			286.770	8886.698	100	0.000	

Figure S27. HPLC curve of (*S*)-2-((*R*)-1-(4-methoxyphenyl)-2-nitroethyl) cyclohexanone (**6ba**) (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 80/20 (v/v); 0.50 mL/min; 254 nm; 25 °C).



No.	Ret. Time min	Peak name	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %	Amount	Type
1	12.562	n.a.	362.721	738.236	43.918	n.a.	BMB*
2	13.674	n.a.	45.903	930.056	5.533	n.a.	BMB*
3	15.622	n.a.	43.656	104.125	6.194	n.a.	BMB*
4	18.832	n.a.	280.458	745.568	44.355	n.a.	BMB*
Total			732.738	168.091	100	0.000	

Figure S28. HPLC curve of racemic (*S*)-2-((*R*)-1-(4-chlorophenyl)-2-nitroethyl) cyclohexanone (**6ca**) (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 90/10 (v/v); 0.50 mL/min; 254 nm; 25 °C).

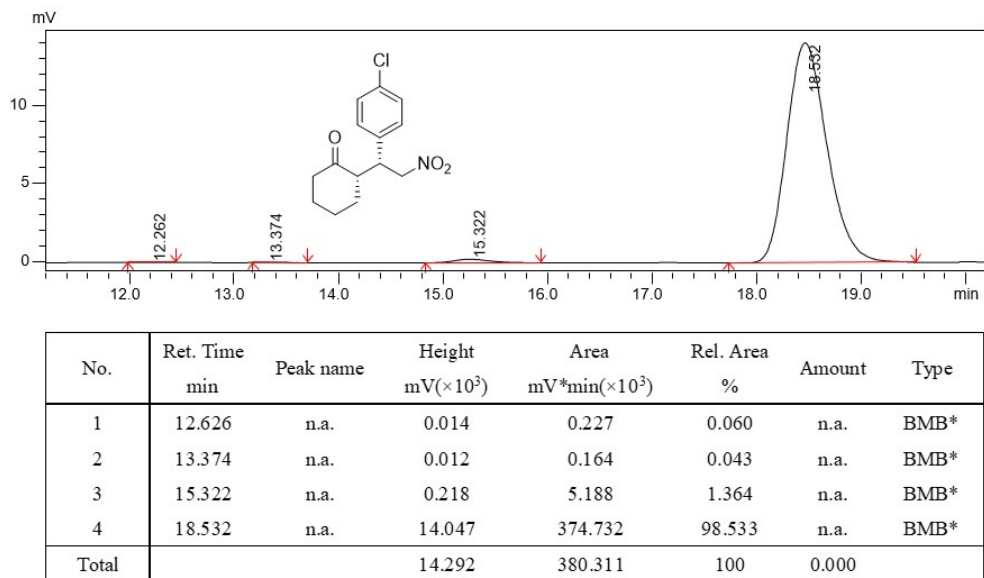


Figure S29. HPLC curve of (*S*)-2-((*R*)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexanone (**6ca**) (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 90/10 (v/v); 1.00 mL/min; 210 nm; 25 °C).

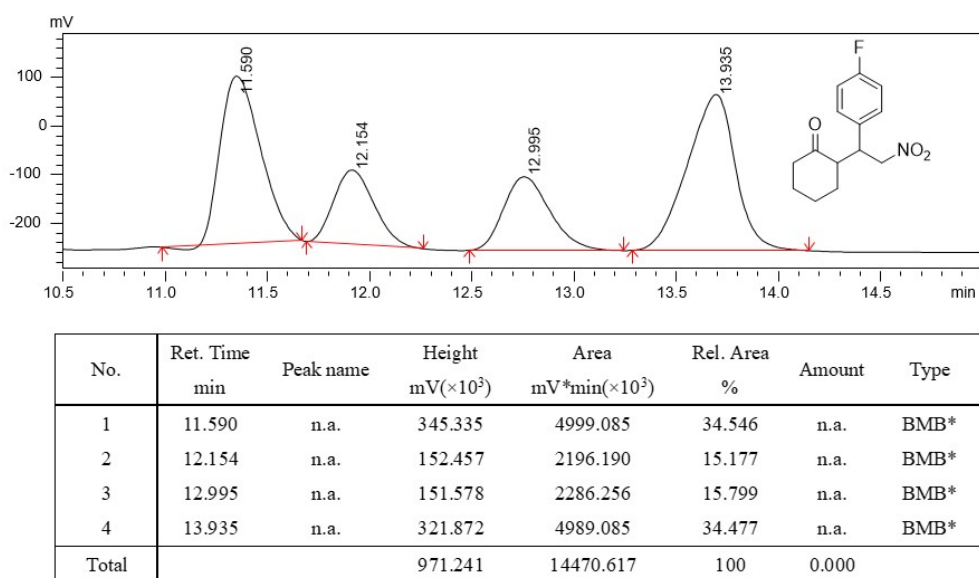
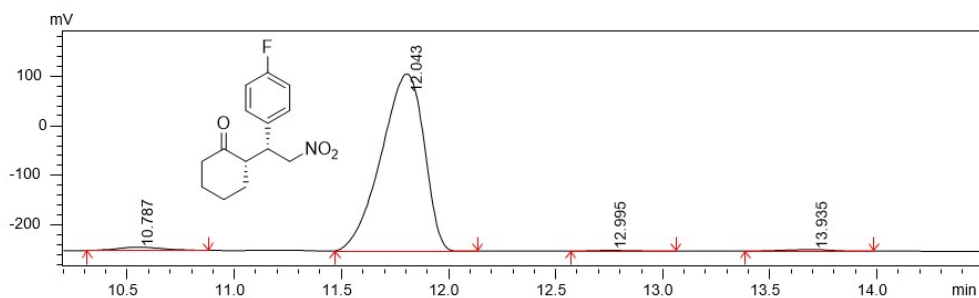
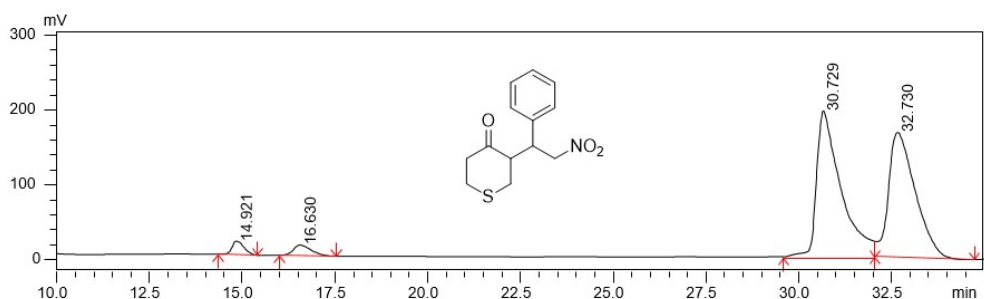


Figure S30. HPLC curve of racemic 1-(4-Fluorophenyl)-2-nitroethyl)cyclohexanone (**6da**) (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 75/25 (v/v); 0.70 mL/min; 254 nm; 25 °C).



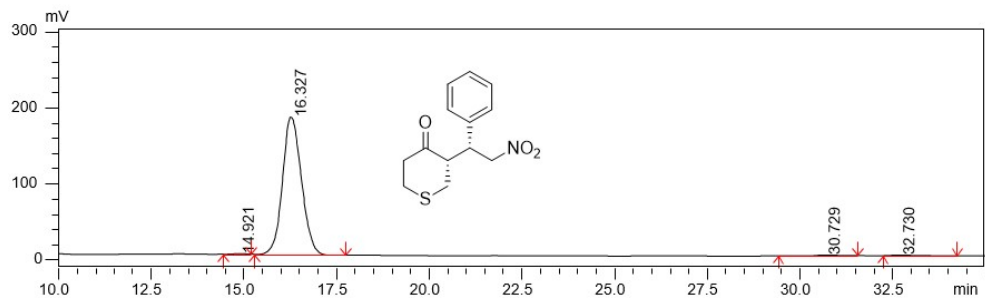
No.	Ret. Time min	Peak name	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %	Amount	Type
1	10.787	n.a.	7.389	111.467	2.154	n.a.	BMB*
2	12.043	n.a.	357.746	4996.148	96.542	n.a.	BMB*
3	12.995	n.a.	1.387	19.757	0.382	n.a.	BMB*
4	13.935	n.a.	3.097	47.727	0.922	n.a.	BMB*
Total			369.618	5175.098	100	0.000	

Figure S31. HPLC curve of (*S*)-2-((*R*)-1-(4-fluorophenyl)-2-nitroethyl)cyclohexanone (**6da**) (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 75/25 (v/v); 0.70 mL/min; 254 nm; 25 °C).



No.	Ret. Time min	Peak name	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %	Amount	Type
1	14.921	n.a.	18.490	417.602	2.283	n.a.	BMB*
2	16.630	n.a.	13.964	470.793	2.573	n.a.	BMB*
3	30.729	n.a.	196.005	8772.725	47.952	n.a.	BMB*
4	32.730	n.a.	166.253	8633.800	47.192	n.a.	BMB*
Total			394.713	18294.920	100	0.000	

Figure S32. HPLC curve of racemic tetrahydro-3-(2-nitro-1-phenylethyl)thiopyran-4-one (**6ab**) (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 85/15 (v/v); 1.00 mL/min; 230 nm; 25 °C)



No.	Ret. Time min	Peak name	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %	Amount	Type
1	14.921	n.a.	0.438	15.576	0.238	n.a.	BMB*
2	16.327	n.a.	182.563	6462.114	99.300	n.a.	BMB*
3	30.729	n.a.	0.441	35.372	0.240	n.a.	BMB*
4	32.730	n.a.	0.408	34.163	0.222	n.a.	BMB*
Total			183.850	6547.226	100	0.000	

Figure S33. HPLC curve of (*S*)-tetrahydro-3-((*R*)-2-nitro-1-phenylethyl)thiopyran-4-one (**6ab**) (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 85/15 (v/v); 0.50 mL/min; 230 nm; 25 °C).

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